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Article

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Quenching of excited triplet states by dissolved natural organic matter

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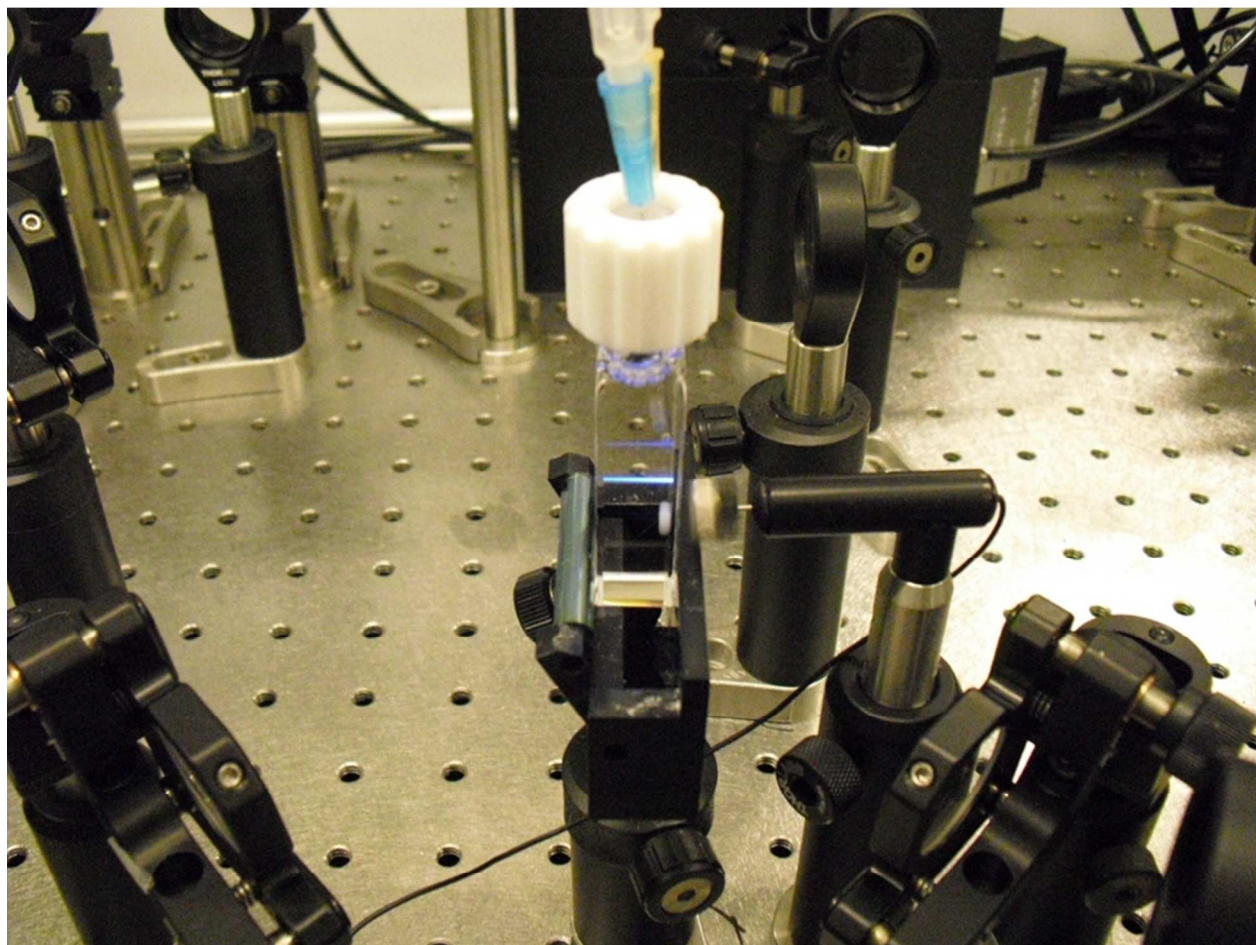
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Abstract

Excited triplet states of aromatic ketones and quinones are used as proxies to assess the reactivity of excited triplet states of the dissolved organic matter ($^3\text{DOM}^*$) in natural waters. $^3\text{DOM}^*$ are crucial transients in environmental photochemistry responsible for contaminant transformation, production of reactive oxygen species and potentially photobleaching of DOM. In recent photochemical studies aimed at clarifying the role of DOM as an inhibitor of triplet-induced oxidations of organic contaminants, aromatic ketones have been used in the presence of DOM, and the question of a possible interaction between their excited triplet states and DOM has emerged. To clarify this issue, time resolved laser spectroscopy was applied to measure the excited triplet state quenching of four different model triplet photosensitizers induced by a suite of DOM from various aquatic and terrestrial sources. While no quenching for the anionic triplet sensitizers 4-carboxybenzophenone (CBBP) and 9,10-anthraquinone-2,6-disulfonic acid (2,6-AQDS) was detected, second-order quenching rate constants with DOM for the triplets of 2-acetonaphthone (2AN) and 3-methoxyacetophenone (3MAP) in the range of $1.30 - 3.85 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ were determined. Based on the average molecular weight of DOM molecules the quenching for these uncharged excited triplet molecules is nearly diffusion-controlled, but significant quenching (>10%) in aerated water is not expected to occur below DOM concentrations of $22 - 72 \text{ mg}_\text{C} \text{ L}^{-1}$.

Introduction

Excited triplet states are important intermediates in the photochemistry of organic molecules.^{1, 2} The photophysical processes leading to their deactivation and the eventual restoration of the ground electronic state of the parent molecule are generally much slower than those affecting their precursors, the excited singlet states. The relatively long lifetimes of excited triplet states is a direct result of the fact that triplet to singlet transitions are spin-forbidden. Thus, once the triplet state is populated, it has sufficient time (typically on the order of microseconds in solution) to undergo bimolecular reactions. In contrast, molecules in their excited singlet state are deactivated on the nanosecond timescale and therefore have little chance of having a fruitful encounter with a reaction partner.

Besides being involved in direct phototransformation reactions of aquatic contaminants,³ excited triplet states are pivotal players in the aquatic photochemistry of dissolved natural organic matter (DOM).^{4, 5} Such triplet states, termed here as $^3\text{DOM}^*$, are considered to be the main precursors of singlet molecular oxygen photoproducts in surface waters,^{6, 7} but may also react directly with various substances present in natural waters. While the first studied reaction directly induced by $^3\text{DOM}^*$ was a photoisomerization following triplet–triplet energy transfer,⁸ later studies focused on the capability of $^3\text{DOM}^*$ to induce the transformation of organic contaminants by oxidation.^{9–12} The variety of aquatic contaminants and natural compounds shown to undergo transformation induced by $^3\text{DOM}^*$ has continued to increase in recent years.^{13–21}

Under the conditions generally encountered in sunlit surface waters, the lifetime of excited triplet states is expected to be controlled either by intramolecular radiationless deactivation or by quenching with dissolved molecular oxygen. The latter situation was shown to occur for the

triplet states of three aromatic ketones, which exhibited lifetimes in the range of 1.2 – 1.6 μs in aerated water.¹⁰ The lifetimes of $^3\text{DOM}^*$ are expected to be highly variable, owing to the complexity of DOM and the presence of various moieties within the same macromolecule, which might be efficient triplet quenchers and accelerate the decay of some $^3\text{DOM}^*$. However, in aerated conditions, there is an upper limit to the triplet lifetime, which is imposed by quenching due to molecular oxygen and should generally not exceed a few microseconds.⁴ Some attempts were made to detect transients resulting from laser flash photolysis of DOM,^{22, 23} but very limited information could be obtained regarding $^3\text{DOM}^*$. The obvious reason is that DOM is too a complex mixture of chromophores to allow the extraction of detailed transient absorption and kinetic data related to its triplet states. An indirect approach using the yield of singlet oxygen production and its dependence on oxygen concentration has recently led to the identification of at least two distinct pools of $^3\text{DOM}^*$ having natural lifetimes (i.e. lifetimes in the absence of oxygen) in water in the range of $\approx 20 - 80 \mu\text{s}$.²⁴

Direct determination of triplet quenching rate constants has been possible for more than half a century by now, but extensive data sets for organic quenchers in nearly pure aqueous solution (with organic co-solvent amount $\leq 2\%$ vol/vol) are still quite sporadic in comparison to those obtained in organic solvents.²⁵ Aqueous second-order quenching rate constants are available for several compounds of biological relevance,²⁶⁻³⁰ substituted phenols¹⁰ and phenylurea herbicides.¹² Maximum rate constants obtained were typically in the range of $\approx 2 - 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which may be considered to be close to the diffusion limit for water as a solvent at room temperature. To date there is no quantitative information about the triplet quenching ability of DOM, although quenching appears to be a realistic possibility owing to the variety of molecular moieties that constitute DOM. There are various timely issues in aquatic photochemistry for which an advance

in knowledge on this topic is critical. A first motivation is derived from our recent studies,³¹⁻³³ in which DOM has been shown, for various organic substances, especially aromatic nitrogen compounds, to reduce their rates of transformation induced by excited triplet aromatic ketones. Based on various considerations^{31, 34} triplet quenching by DOM was excluded as a reason for the observed inhibited transformation, but a direct measurement would add strong evidence for or against this hypothesis. Second, the use of photosensitizers is a possible option for the elimination of chemical and biological contaminants from surface waters and wastewaters. To evaluate the effectiveness of such treatment processes and to estimate its possible impact on the transformation of DOM, the extent of quenching of the excited triplet photosensitizer by DOM is an important piece of knowledge. Third, there is an interest in clarifying the role of DOM itself as a quencher of $^3\text{DOM}^*$ and in assessing to what extent self-photosensitization may contribute to the transformation of DOM.

The objective of this study is to possibly detect and quantify the DOM-induced quenching of the excited triplet states of a few photosensitizers. Aqueous solutions containing the aromatic ketones benzophenone-4-carboxylate, 2-acetonaphthone and 3-methoxyacetophenone, and the aromatic quinone 9,10-anthraquinone-2,6-disulfonate, were submitted to laser flash photolysis in the presence and absence of several dissolved DOM extracts. The selected photosensitizers, chosen mainly based on our previous studies, have oxidizing excited triplet states and triplet energies in the range of $249 - 303 \text{ kJ mol}^{-1}$ ($2.6 - 3.2 \text{ eV}$).³⁵ Their possible interactions with DOM include oxidative quenching of (mainly phenolic) antioxidant moieties as well as triplet-triplet energy transfer to chromophoric moieties.

Experimental Section

Chemicals and preparation of solutions. All chemicals were from commercial sources and used as received. Excited triplet state sensitizers: 2-acetonaphthone (2AN) [CAS 93-08-3] >99%, 3-methoxyacetophenone (3MAP) [586-37-8] 97%, 4-carboxybenzophenone (CBBP) [611-95-0] >99%, 9,10-anthraquinone-2,6-disulfonic acid disodium salt (2,6-AQDS) [853-68-9] $\geq 97\%$, all Sigma-Aldrich. Excited triplet state model quencher: 2,4,6-trimethylphenol (TMP) [527-60-6] (EGA Chemie, 99%).

Humic and fulvic acid isolates: Leonardite humic acid standard (Catalog number 1S104H, LHA), Nordic aquatic fulvic acid reference (1R105F, NAFA), Nordic reservoir NOM (1R108N, NRNOM), Pahokee Peat humic acid reference (1R103H, PPHAR), Pahokee Peat humic acid standard (1S103H, PPHAS), Pony Lake fulvic acid reference (1R109F, PLFA), Suwannee River fulvic acid standard II (2S101F, SRFA), Suwannee River humic acid standard (2S101H, SRHA), Suwannee River NOM (1R101N, SRNOM), Waskish Peat humic acid reference (WPHAR), were obtained from the International Humic Substances Society (IHSS).

All aqueous solutions were prepared from ultrapure water (resistivity $>18 \text{ M}\Omega \text{ cm}$) obtained from Milli-Q (Millipore) or Barnstead water purification systems. Humic and fulvic acid stock solution ($\sim 200 \text{ mg}_\text{C} \text{ L}^{-1}$) were prepared in phosphate buffer (10mM, pH7). The DOM concentration of the stock solutions was determined, after appropriate dilution, as organic carbon using a Shimadzu V-CPH TOC analyzer (Kyoto, Japan). Prior to spectroscopic measurements DOM solutions were diluted with phosphate buffered water (10 mM, pH 6-10, majority of measurements pH 7) to $0.5 - 35 \text{ mg}_\text{C} \text{ L}^{-1}$ ($0.041 - 2.92 \text{ mmol}_\text{C} \text{ L}^{-1}$) and spiked with triplet sensitizers from methanol (2AN, CBBP, 3MAP, all 0.1M) or aqueous (2,6-AQDS) stock solutions to yield final concentrations of $300 \mu\text{M}$ (2AN) and $500 \mu\text{M}$ (2,6-AQDS, CBBP, 3MAP), respectively. The presence of methanol

in the aerated aqueous sample solutions at a maximum concentration of 0.5 % vol/vol was previously shown not to affect the triplet lifetimes of the studied ketones.¹⁰ A blank sample without DOM containing the respective sensitizer in buffered water only was measured for every series of each DOM. pH measurements were carried out at room temperature on a Metrohm pH meter model 632 (Herisau, Switzerland) or a portable device HANNA HI 99104 (HANNA instruments, Smithfield, RI).

Laser spectroscopy. Time-resolved measurements were obtained via pump-probe transient absorption spectroscopy. The pump laser pulse was generated by a Solstice amplified Ti:Sapphire ultrafast laser (Newport Spectra-Physics, Darmstadt, Germany). 795 nm pulses (3.2 watt, 80 fs fwhm) were directed into a Topas optical parametric amplifier for wavelength conversion (Light Conversion, Vilnius, Lithuania). The output was tuned to generate an optimal pump wavelength for excitation of the selected sensitizer (CBBP @ 300 nm, 2AN @ 350 nm and @ 325 nm in quenching experiments with TMP, 3-MAP and 2,6-AQDS @ 325 nm). The modified laser pulse was then steered into an EOS transient absorption spectrometer (Ultrafast Systems, Sarasota, Florida) where it was collimated and focused (~ 1 mm spot size) onto a 1 cm quartz cuvette (Starna Scientific Ltd, Essex, UK). The pump and probe beams converge at the cuvette at a shallow angle to maximum pump-probe overlap, maximizing the effective path length (~ 5 mm). The probe beam consists of a Nd:YAG laser directed into an optical fiber waveguide to generate a supercontinuum pulse (~ 365 – 1700 nm, ~ 1 ns fwhm). The probe beam is triggered via TTL pulses from the EOS software to sample different time slices past time zero. The probe beam is split into a signal and reference beam to automatically compensate for intensity variation in the probe. The signal and reference beams are then focused into separate fiber optic inputs each connected to a CCD array spectrometer (365 – 800 nm working range). The inherent time resolution of the instrument is in the sub-nanosecond range, however the Δt time window can be

optimized for the collection of short-lived excited singlet species, or longer-lived triplet states. For this study we optimized both the time window and resolution to provide the highest quality data for the target triplet state lifetimes. Thus, although the kinetic traces of the singlet precursors can be obtained with this instrument, we did not focus on these species. The resulting data consists of a three dimensional array of wavelength, ΔAbs and Δt . Data analysis was performed with the Surface Explorer software package (Ultrafast Systems, Sarasota, Florida) and Origin 8.5 (OriginLab, Northampton, MA). The spectroscopic array data was first corrected for any background and scattered laser light present. Then individual transient decays were extracted and fit to a single exponential function to determine relaxation times. Triplet decays for the sensitizers were determined at the following wavelengths: 2AN (440 nm), CBBP (415 nm and 550 nm), 3-MAP (395nm), 2,6-AQDS (390nm and 610nm). The data for the 2,6-AQDS samples was especially complicated and difficult to fit following the procedure outlined above. For these samples the data was processed using a three component singular value decomposition algorithm.³⁶ The data was then reconstructed from these extracted components and fit to a biexponential decay.

All samples were purged with synthetic air (80% N₂, 20% O₂; Carbagas, Zurich, Switzerland) before and during measurements and were stirred continuously using a magnetic stirring system (Ultrafast Systems, Sarasota, Florida). For measurements in absence of oxygen samples were purged with argon (purity 5.0, Carbagas).

Results and Discussion

Transient absorption spectroscopy. Figure 1 shows normalized data matrices of laser beam-excited photosensitizers in aqueous solution. Time-resolved spectral data were recorded for

solutions containing no additional component and DOM (SRHA or SRFA) as a possible quencher, respectively. For all employed photosensitizers, clear transient absorption signals in the microsecond time range were obtained. Both photo-excited 2AN (Figure 1a) and 3MAP (Figure 1b) exhibit a single band spectrum with an absorption maximum at 440 nm and 400 nm, respectively, in agreement with published triplet-triplet absorption spectral data.^{37, 38} The presence of DOM (at a concentration of 27 – 33 mg_C L⁻¹) slightly affects the shape of the spectral bands (in the case of 3MAP, a small red shift and the formation of a shoulder at ≈430 nm are observed). These spectral changes are too small to allow an assignment to possible transients formed upon triplet quenching. Moreover, they cannot be compared to the clear changes obtained in the presence of TMP, a well-known phenolic quencher (see Figure 2). For the two other photosensitizers, spectra are more complex but appear to be unaffected by the presence of DOM. The spectrum of CBBP (Figure 1c) reveals two maxima at 415 nm and 550 nm and can also be assigned exclusively to the absorption of excited triplet CBBP. The position of the first maximum is affected by the reduced intensity of the probe beam source in the UV range (the actual band maximum is clearly below 390 nm).^{39, 40} However, this is irrelevant for the measurement of the decay kinetics of the triplet state. Spectra and decay curves for 2,6-AQDS (Figure 1d) possess an initial fast decaying component and a longer-lived species (half-life longer than the observation time). Moreover for 2,6-AQDS, concomitantly with the decay of the component with absorption maximum at 390 nm, an additional band with a maximum absorption at 610 nm appeared. Such a component was assigned previously to 2,6-AQDS-water adducts formed from excited triplet 2,6-AQDS.^{41, 42}

As expected by the choice of the observation time frame (see Experimental Section) no excited singlet states evolving from the ground state were observed. For the sensitizers used here these

206 singlet states are very short-lived (e.g. 2AN, 0.19 ns⁴³). The extremely short lifetimes and high
207 triplet yields of the sensitizers (see ϕ_{ISC} Table 1) effectively rule out possible interactions between
208 DOM and the sensitizers in the singlet state, unless they were associated prior to excitation.
209 Triplet lifetimes for all sensitizers were determined by exponential fitting as described above and
210 are given in Table 1. Differences between lifetimes reported here and those reported in the
211 literature for both synthetic air and argon purged samples are generally within the uncertainty of
212 the measurements and are likely due to different [O₂] (i.e. in open cells where ambient conditions
213 might affect oxygen levels) or impurities of the sensitizers and buffer solutions employed.
214 However, the critical issue for this work is the consistency of the experiment between samples
215 within the same series. Careful attention to this factor was paid and variations in triplet lifetimes
216 among measurements performed at different days during the data collection period were found to
217 be negligible indicating that quenching values do not suffer from external influences.

218 Table 1. Lifetimes and rate constants for the excited triplet photosensitizers

	2-AN	CBBP	3MAP	AQDS
CAS-RN	93-08-3	2215-77-2	586-37-8	853-68-9
E_T (kJ/mol) ^a	249 ⁴⁴	286 ⁴⁰	303 ⁴⁴	259 ³⁵
$E_{red}^{0'}$ (V vs. NHE) ^b	-1.72 ⁴⁵	-1.13 ⁴⁰	-1.81 ⁴⁶	-0.535 ⁴⁷
$E_{red}^{0'}(triplet)$ (V vs. NHE) ^c	1.10	1.83	1.57	2.39
ϕ_{ISC}^d	0.84 ⁴⁸	1 ⁴⁰	1 ¹⁰	
τ_{TD} (aerated, μ s, literature)	1.55 ± 0.03 ¹⁰	3 ⁴⁹	1.19 ± 0.08 ¹⁰	0.36 ⁴¹
τ_{TD} (deaerated, μ s, literature)	18.4 ⁵⁰	12 ± 2 ⁴⁰	3.1 ³⁸	
τ_{TD} (aerated, μ s, this work)	1.588 ± 0.095^e	2.153 ± 0.030^f	1.315 ± 0.007^g	0.600 ± 0.054 ; 2.030 ± 0.273^h
τ_{TD} (deaerated, μ s, this work)	10.93 ± 0.98^i	15.54 ± 2.32		
k_{TQ}^{DOM} (L mol ⁻¹ s ⁻¹) ^{j, k}	2-AN	CBBP	3MAP	AQDS
TMP (literature) ¹⁰	$(7.2 \pm 0.1) \times 10^8$		$(2.6 \pm 0.3) \times 10^9$	
TMP (this work)	$(6.17 \pm 0.16) \times 10^8$		$(1.88 \pm 0.21) \times 10^9$	
SRFA	$(3.47 \pm 0.50) \times 10^7$	$< 1 \times 10^7$	$(2.47 \pm 0.59) \times 10^7$	nd ^l
NAFA	$(1.60 \pm 0.29) \times 10^7$	nd		nd
PLFA	$(1.97 \pm 0.24) \times 10^7$	nd	$(1.41 \pm 0.37) \times 10^7$	nd
WPHAR	$(3.85 \pm 0.20) \times 10^7$	nd		nd
LHA	$(1.44 \pm 0.20) \times 10^7$			nd
PPHAS	$(2.09 \pm 0.42) \times 10^7$			
SRNOM	$(1.92 \pm 0.25) \times 10^7$			
NAHA	$(2.25 \pm 0.16) \times 10^7$			
PPHAR	$(1.90 \pm 0.17) \times 10^7$			
SRHA	$(1.30 \pm 0.63) \times 10^7$			

219 ^aEnergy of the excited triplet state relative to the electronic ground-state. ^bStandard one-electron reduction potential of the electronic
220 ground-state (unit: V vs. normal hydrogen electrode (NHE)). ^cStandard one-electron reduction potential of the excited triplet state
221 calculated as $E_{red}^{0'} + E_T/F$ ¹⁰; F : Faraday constant (9.6485×10^4 A s mol⁻¹). ^dExcited singlet–triplet intersystem crossing quantum
222 yield. ^eStandard deviation of 15 measurements at 440 nm. ^fStandard deviation of 6 measurements at 550 nm. ^gStandard deviation of 2

223 measurements at 395 nm. ^hStandard deviation of 5 measurements at 390 nm; AQDS shows biexponential decay kinetics. ⁱStandard
224 deviation of 2 measurements at 440 nm. ^jObtained from measurements in aerated solution (see text). ^kFor TMP: k_{TQ}^{TMP} (M⁻¹s⁻¹). ^l*nd*:
225 Quenching not detected above the level of uncertainty.

Signal disturbances by DOM are expected to be little (for effects of light attenuation by DOM see next sub-section). Preliminary experiments with several DOM revealed the occurrence of a broad absorption band with maximum between 600 and 700 nm, probably due to the formation of solvated electrons.⁵¹ However, these experiments, conducted with the aim to detect any transient formed from DOM, were performed at much higher energy density (tightly focused pump beam (~ 0.5 mm) and pulse energy > 10 mW) than quenching experiments. Under the conditions used for quenching experiments, only a very low maximum ΔAbs was recorded for DOM blanks (e.g., 0.0020 for WPHAR, 0.0025 for PLFA, 0.004 for NAHA, see also SI Figure S1), and we can safely assume that effects from these weak transients can be ignored in the analysis of the data.

In contrast to DOM, addition of TMP, which is a well-known and effective quencher of excited triplet states,¹⁰ leads to a significant change of the signal pattern obtained for 2AN and 3MAP (Figure 2). In both cases the triplet signal is strongly decreased at short time delays after the pulse and formation of transient species with absorption maxima at 390-400 nm is observed. Such species potentially correspond to the ketyl radical of the photosensitizer and the phenoxyl radical of TMP, which are believed to be formed during oxidation of TMP by the excited triplet.¹⁰ While the ketyl radical should be depleted by reacting with O_2 to give the superoxide anion on a time scale of a few μs (e.g. 1.7 μs for benzophenone in aerated solution),¹⁰ the phenoxyl radical should be much longer lived. For 2AN the observed lifetime of the feature at 390 nm was 96 ± 10 μs (Ar-purged) and 2.88 ± 0.37 μs (synthetic air), indicating the ketyl radical. For 3MAP the observed lifetime of such a species at 400 nm was 1.82 ± 1.06 μs (synthetic air). However, this measurement was hampered by the overlap with the parent sensitizer triplet signal.

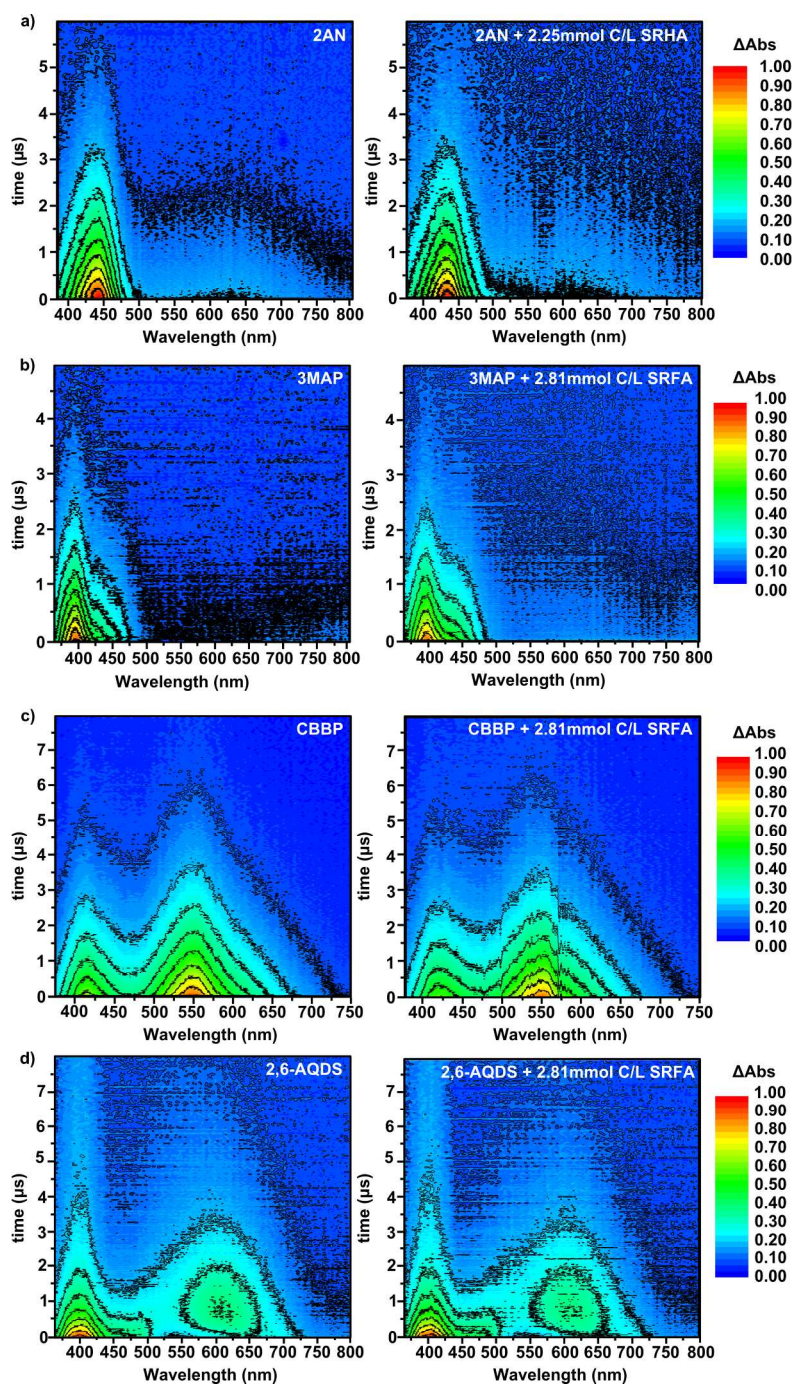


Figure 1. Normalized 2-D contour plots of representative transient absorption data in 10 mM phosphate buffered water at pH 7 (left hand side each figure) and in presence of DOM (right-hand side each figure). Colors indicate the scale of differential absorbance, ΔAbs (normalized independently for each plot).

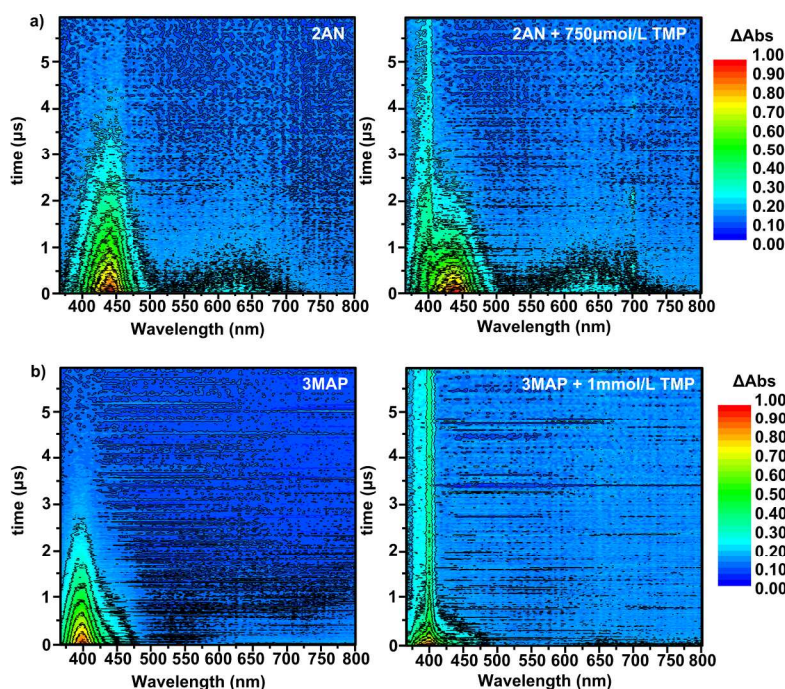


Figure 2. Normalized 2-D contour plots of transient absorption data in 10 mM phosphate buffered water at pH 7 (left hand side each figure) and in presence of TMP (right-hand side each figure). Colors indicate the scale of differential absorbance, ΔAbs (normalized independently for each plot).

Quenching rate constants

For an exact quantification of the quenching effect on excited triplet states, series of transient absorption measurements using various DOM concentrations were conducted. A representative series of decay curves at 440 nm for the couple 2AN/SRFA is shown in Figure 3a. With increasing DOM concentration a decline in signal quality due to intrinsic light absorption by DOM (decreasing maximum ΔAbs , increasing scattering and limiting the investigable concentrations for most of DOM to $\sim 3 \text{ mmol}_c \text{ L}^{-1}$, i.e., $\sim 36 \text{ mg}_c \text{ L}^{-1}$) was observed that depends on the type of DOM (Absorption: PLFA < NAFA < NRNOM < SRFA < SRNOM < SRHA < PPHAR < PPHAS < WPHAR < LHA). Visual inspection of the decay curves indicated that the

lifetime of excited triplet states remains unchanged or decreased only marginally with DOM concentration.

The relaxation of an excited triplet state in solution may be described by the following equation (in analogy to the formalism used by Wilkinson and coworkers⁵²):

$$k_{TD} = k_{TD}^0 + k_{TQ}^{O_2}[O_2] + k_{TQ}^{DOM}[DOM] \quad (1)$$

k_{TD} (s^{-1}) is the first-order relaxation rate constant of the excited triplet state and includes the contributions of all unimolecular and solvent-induced relaxation channels, summarized by k_{TD}^0 , as well as the bimolecular contributions induced by quenchers, in the present case molecular oxygen and DOM, $k_{TQ}^{O_2}$ and k_{TQ}^{DOM} being the corresponding second-order quenching rate constants, respectively. Note that the triplet lifetime corresponds to the inverse of the relaxation rate constant: $\tau_{TD} = (k_{TD})^{-1}$. Results for various quenching experiments are shown in Figure 3b – d as simple Stern-Volmer-plots of $(\tau_{TD})^{-1}$ vs. the concentration of DOM, while the concentration of the other quencher, i.e. molecular oxygen, is kept constant during the individual experimental series. Figure 3b shows plots for 2AN and CBBP in aerated and deaerated solutions. Linear regression analysis of the Stern-Volmer plots yields the desired second-order quenching rate constant, k_{TQ}^{DOM} , as the slope, and the relaxation rate constant in the absence of DOM, $k_{TD}^0 + k_{TQ}^{O_2}[O_2]$, as the intercept of the regression line.

A summary of the determined rate constants is given in Table 1. We first consider the triplet lifetimes obtained in the absence of DOM. As expected according to equation 1, lifetimes are higher (and first-order relaxation rate constants lower) in oxygen-poor solutions (Ar-purged) than in aerated solutions. To determine second-order quenching rate constants by DOM, series in both aerated and Ar-purged solutions were performed (and yielded comparable rate constants), with

the initial expectation of an improved quantification in the latter case owing to higher fractional changes in lifetime upon DOM addition. However, measurements in aerated solutions turned out to be more robust due to a lesser interference by secondary transients, and so the majority of measurements were conducted in aerated solutions. Among the four tested sensitizers we were able to determine a set of second-order quenching rate constants for 2AN and 3MAP. Constants are in the range of $(1.30 - 3.85) \times 10^7 \text{ L mol}_C^{-1} \text{ s}^{-1}$ for 2AN and of $(1.41 - 2.47) \times 10^7 \text{ L mol}_C^{-1} \text{ s}^{-1}$ for 3MAP, respectively. Considering the relatively high molecular weight of DOM, these values have to be multiplied by about two orders of magnitude to give second-order rate constants on a molar base (for instance, SRFA contains 52% carbon and has an average molecular weight of 2310 g mol^{-1} ,⁵³ which means that an SRFA molecule consists of 100 carbon atoms on average). Such estimated rate constants ($\approx (1.3 - 3.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are not far from the apparent diffusion limit of $\approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ obtained for electron transfer reactions to excited triplet states of aromatic ketones in aqueous solution,^{10, 12} and thus similar to (or, in the case of 2AN even higher than) the second-order quenching rate constants for TMP. One can conclude that DOM is indeed a very effective quencher of excited triplet 2AN and 3MAP on a molar basis, but, owing to the high average size of its molecules, a high amount of it (in terms of weight) is required to produce significant quenching (see next sub-section). Another important observation is that the DOM quenching rate constants for 2AN and 3MAP are not very different, while one would expect a higher quenching rate with 3MAP due to its higher triplet energy and one-electron reduction potential (the latter explains why TMP quenches excited triplet 3MAP more efficiently than excited triplet 2AN¹⁰, see also Table 1 and SI, Figure S2). This fact, together with the almost diffusion-controlled rates, suggests that within a single DOM (macro)molecule very efficient triplet quencher moieties are present, which may react through other quenching mechanisms than

electron-rich phenols. Candidates for such additional quenching moieties are chromophoric components of the DOM acting as acceptors of electronic excitation energy in triplet–triplet energy transfer processes.

The barely measurable quenching of excited triplet CBBP and the absence of quenching in the case of 2,6-AQDS are probably amenable to the negative electric charge borne by the photosensitizer molecules and the consequent repulsion against the negatively charged DOM molecules. This repulsion is expected to hinder the encounter of these anionic excited triplet photosensitizers with quenching moieties of DOM molecules. By inspecting the parameters given in Table 1 it is clear that neither the energy nor the reduction potential of the excited triplet state can account for the strongly reduced quenching rates of the negatively charged species.

To account for the pH range occurring in natural waters and to potentially gain some mechanistic insights into the quenching process, we performed a series of pH-dependent experiments (Figure 3 d). Within the uncertainty of measurements the quenching effect shows independence from pH for both 2AN and CBBP. These data suggest that the quenching rates are unaffected by the protonation state of the DOM molecules and supports the just mentioned suggestion that phenolic moieties are not the main triplet quenchers in the DOM.

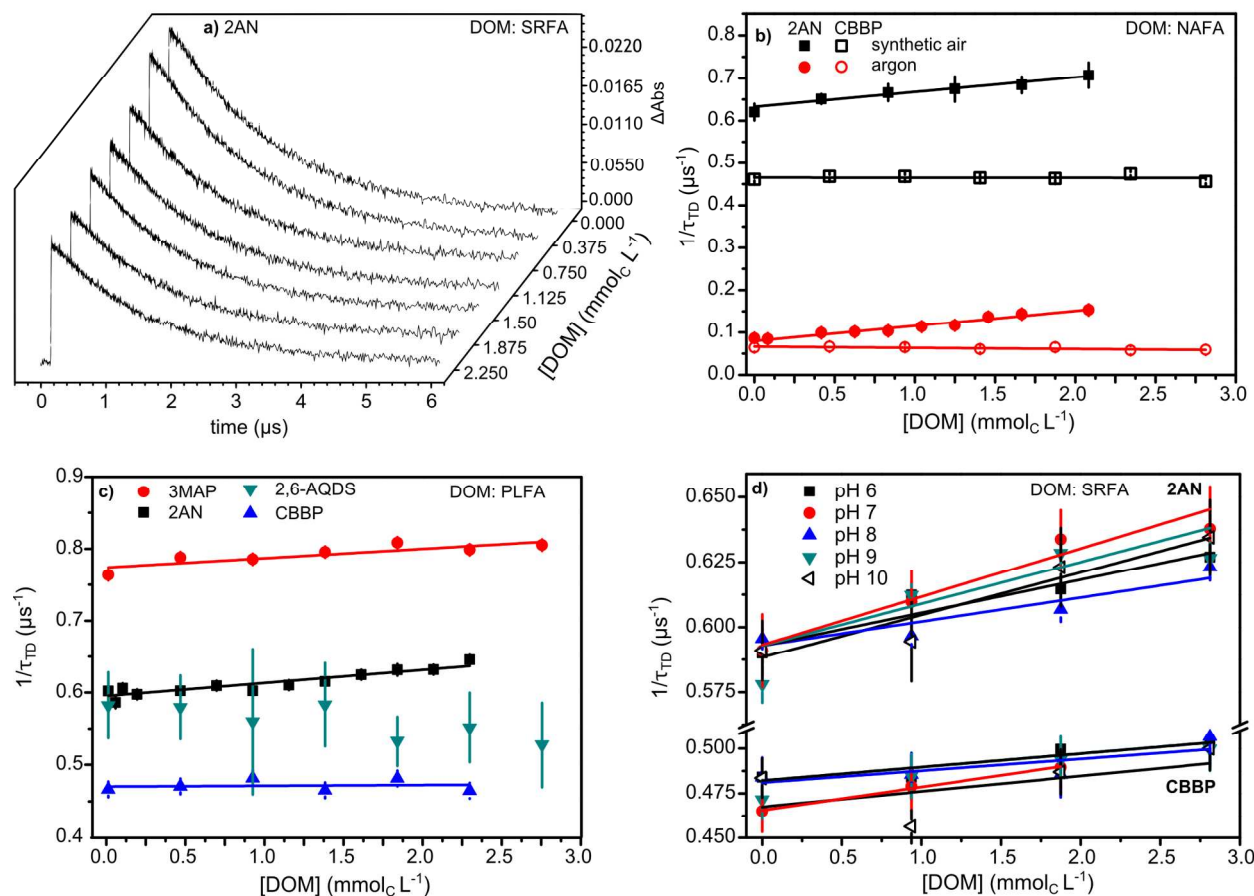


Figure 3. (a) Transient absorption decay curves of $^3\text{2AN}^*$ at 440 nm with increasing DOM (SRFA) concentration ($\Delta\text{Abs}(t) = \text{Abs}(t)_{\text{sample}} - \text{Abs}(t)_{\text{blank}}$). (b) Inverse lifetimes of $^3\text{2AN}^*$ and $^3\text{CBBP}^*$ vs. DOM (NAFA) concentration in synthetic air and argon purged aqueous solutions (10 mM phosphate buffer, pH 7). (c) Inverse lifetimes of the excited triplet state of four different sensitizers with increasing DOM (PLFA) concentration. (d) Inverse lifetimes of $^3\text{2AN}^*$ and $^3\text{CBBP}^*$ vs. DOM (SRFA) concentration at pH 6 – 10. Error bars indicate 95% confidence intervals of data fits. In some cases error bars are smaller than data points.

Implications for aquatic photochemistry

The quenching of the excited triplet states of the selected photosensitizers brought about by DOM may be considered as relatively small under the conditions of aerated water, which is prevalent for most sunlit surface waters. To be noted is that under steady-state irradiation, as is the case for solar illumination, a reduction in excited triplet state lifetime quantitatively corresponds to a reduction in excited triplet state concentration, and consequently in the rate constant for triplet-induced transformation of a hypothetical trace contaminant. In this study, the quenching of the triplet states of anionic photosensitizers (CBBP and 2,6-AQDS) could not be quantified owing to its small extent. In contrast, the two photosensitizers present as neutral species (2AN and 3MAP) exhibited a measurable quenching. Using the second-order rate constants given in Table 1, one can assess the DOM concentration needed, for each DOM and each photosensitizer, to reduce the excited triplet lifetime by, for instance, 10%. For such a case, one can write the following equation:

$$\frac{k_{TD}^0 + k_{TQ}^{O_2}[O_2]}{k_{TD}^0 + k_{TQ}^{O_2}[O_2] + k_{TQ}^{DOM}[DOM]} = 0.9 \quad (2)$$

Solving for the DOM concentration one obtains:

$$[DOM]_{-10\%} = \frac{k_{TD}^0 + k_{TQ}^{O_2}[O_2]}{9k_{TQ}^{DOM}} \quad (3)$$

For all second-order quenching rate constants determined in this study, corresponding $[DOM]_{-10\%}$ values are gathered in SI Table S1. They vary from 1.8 to 6.0 mmol_C L⁻¹, corresponding to 22 – 72 mg_C L⁻¹. From these calculations one can immediately conclude that below such DOM concentrations no significant quenching of the excited triplet states of the photosensitizers occurs. This was a basic assumption, backed by various pieces of indirect evidence, that we proposed in the frame of our previous works on the DOM-induced inhibition of

triplet-induced transformation of organic contaminants.^{31, 32, 34} This assumption is now reinforced based on experimental facts: Dynamic quenching of excited triplet states does not occur significantly at DOM concentrations of a few $\text{mg}_C \text{ L}^{-1}$. For the studied photosensitizers we exclude static quenching, possibly resulting from formation of photosensitizer–DOM complexes in the ground electronic state, because of their low hydrophobicity and the absence of a positive charge.

With the above calculations and the very reduced amount of quenching observed for anionic photosensitizers in mind, it appears very unlikely that intermolecular reactions involving $^3\text{DOM}^*$ may play a role in the photoinduced chemical modification of DOM (often referred to as photobleaching⁵⁴). On the other hand, reactions between $^3\text{DOM}^*$ and a quencher within the same DOM molecule should be possible, but their importance is still unknown.

The application of photosensitizers for water disinfection and contaminant removal has attracted the interest of various scientists for many decades.⁵⁵⁻⁶² From the results of the present study one can conclude that anionic or neutral hydrophilic photosensitizers will hardly be affected by excited triplet state quenching in the presence of DOM. Thus, reactions induced directly or indirectly (as in the case of singlet molecular oxygen) by the excited triplet states of these photosensitizers are not expected to be attenuated by the presence of DOM, except for the cases in which competition for light absorption (inner filter effect) plays a role. Clearly, cationic and neutral hydrophobic photosensitizers will tend to associate with DOM, and the influence of DOM on their effectiveness cannot be predicted from the results of this study.

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Notes

The authors declare no competing financial interests.

Supporting Information Available

2 figures and 1 table address additional data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References

1. Klán, P.; Wirz, J. *Photochemistry of organic compounds. From concepts to practice*. John Wiley & Sons Ltd: Chichester, UK, 2009.
2. Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Modern molecular photochemistry of organic molecules*. University Science Books: Sausalito, CA, USA, 2010.
3. Kouras-Hadef, S.; de Sainte-Claire, P.; ter Halle, A.; Amine-Khodja, A.; Richard, C. The role of triplet state keto-enol tautomerism in the photodeamination of metamitron. *J. Phys. Chem. A* **2011**, *115* (50), 14397-14406.
4. Richard, C.; Canonica, S. Aquatic phototransformation of organic contaminants induced by coloured dissolved natural organic matter. In *The Handbook of Environmental Chemistry*, Hutzinger, O., Ed. Springer: Berlin, Germany, 2005; Vol. 2, Part M, pp 299-323.
5. Canonica, S. Oxidation of aquatic organic contaminants induced by excited triplet states. *Chimia* **2007**, *61* (10), 641-644.
6. Zepp, R. G.; Wolfe, N. L.; Baughman, G. L.; Hollis, R. C. Singlet oxygen in natural waters. *Nature* **1977**, *267* (5610), 421-423.
7. Zafiriou, O. C.; Jousot-Dubien, J.; Zepp, R. G.; Zika, R. G. Photochemistry of natural waters. *Environ. Sci. Technol.* **1984**, *18* (12), A358-A371.

8. Zepp, R. G.; Schlotzhauer, P. F.; Sink, R. M. Photosensitized transformations involving electronic energy transfer in natural waters - Role of humic substances. *Environ. Sci. Technol.* **1985**, *19* (1), 74-81.
9. Canonica, S.; Jans, U.; Stemmler, K.; Hoigné, J. Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones. *Environ. Sci. Technol.* **1995**, *29* (7), 1822-1831.
10. Canonica, S.; Hellrung, B.; Wirz, J. Oxidation of phenols by triplet aromatic ketones in aqueous solution. *J. Phys. Chem. A* **2000**, *104* (6), 1226-1232.
11. Gerecke, A. C.; Canonica, S.; Müller, S. R.; Schärer, M.; Schwarzenbach, R. P. Quantification of dissolved natural organic matter (DOM) mediated phototransformation of phenylurea herbicides in lakes. *Environ. Sci. Technol.* **2001**, *35* (19), 3915-3923.
12. Canonica, S.; Hellrung, B.; Müller, P.; Wirz, J. Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones. *Environ. Sci. Technol.* **2006**, *40* (21), 6636-6641.
13. Chin, Y. P.; Miller, P. L.; Zeng, L. K.; Cawley, K.; Weavers, L. K. Photosensitized degradation of bisphenol A by dissolved organic matter. *Environ. Sci. Technol.* **2004**, *38* (22), 5888-5894.
14. Boreen, A. L.; Arnold, W. A.; McNeill, K. Triplet-sensitized photodegradation of sulfa drugs containing six-membered heterocyclic groups: Identification of an SO₂ extrusion photoproduct. *Environ. Sci. Technol.* **2005**, *39* (10), 3630-3638.
15. Werner, J. J.; McNeill, K.; Arnold, W. A. Environmental photodegradation of mefenamic acid. *Chemosphere* **2005**, *58* (10), 1339-1346.
16. Boreen, A. L.; Edhlund, B. L.; Cotner, J. B.; McNeill, K. Indirect photodegradation of dissolved free amino acids: The contribution of singlet oxygen and the differential reactivity of DOM from various sources. *Environ. Sci. Technol.* **2008**, *42* (15), 5492-5498.
17. Guerard, J. J.; Chin, Y. P.; Mash, H.; Hadad, C. M. Photochemical fate of sulfadimethoxine in aquaculture waters. *Environ. Sci. Technol.* **2009**, *43* (22), 8587-8592.
18. Guerard, J. J.; Miller, P. L.; Trouts, T. D.; Chin, Y. P. The role of fulvic acid composition in the photosensitized degradation of aquatic contaminants. *Aquat. Sci.* **2009**, *71* (2), 160-169.
19. Ryan, C. C.; Tan, D. T.; Arnold, W. A. Direct and indirect photolysis of sulfamethoxazole and trimethoprim in wastewater treatment plant effluent. *Water Res.* **2011**, *45* (3), 1280-1286.
20. Kelly, M. M.; Arnold, W. A. Direct and indirect photolysis of the phytoestrogens genistein and daidzein. *Environ. Sci. Technol.* **2012**, *46* (10), 5396-5403.
21. Felcyn, J. R.; Davis, J. C. C.; Tran, L. H.; Berude, J. C.; Latch, D. E. Aquatic photochemistry of isoflavone phytoestrogens: Degradation kinetics and pathways. *Environ. Sci. Technol.* **2012**, *46* (12), 6698-6704.
22. Fischer, A. M.; Winterle, J. S.; Mill, T. Primary photochemical processes in photolysis mediated by humic substances. **1987**, *327*, 141-156.
23. Power, J. F.; Sharma, D. K.; Langford, C. H.; Bonneau, R.; Jousset-Dubien, J. Laser flash photolytic studies of a well-characterized soil humic substance. *ACS Symposium Ser.* **1987**, *327*, 157-173.

24. Sharpless, C. M. Lifetimes of triplet dissolved natural organic matter (DOM) and the effect of NaBH₄ reduction on singlet oxygen quantum yields: Implications for DOM photophysics. *Environ. Sci. Technol.* **2012**, *46* (8), 4466-4473.
25. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of photochemistry*. 3rd rev. and expanded ed.; CRC Press: Boca Raton, FL, USA, 2006.
26. Encinas, M. V.; Lissi, E. A.; Olea, A. F. Quenching of triplet benzophenone by vitamins E and C and by sulfur-containing amino acids and peptides. *Photochem. Photobiol.* **1985**, *42* (4), 347-352.
27. Encinas, M. V.; Lissi, E. A.; Vasquez, M.; Olea, A. F.; Silva, E. Photointeraction of benzophenone triplet with lysozyme. *Photochem. Photobiol.* **1989**, *49* (5), 557-563.
28. Bobrowski, K.; Marciniak, B.; Hug, G. L. 4-Carboxybenzophenone-sensitized photooxidation of sulfur-containing amino acids – Nanosecond laser flash photolysis and pulse radiolysis studies. *J. Am. Chem. Soc.* **1992**, *114* (26), 10279-10288.
29. Marciniak, B.; Bobrowski, K.; Hug, G. L.; Rozwadowski, J. Photoinduced electron transfer between sulfur-containing carboxylic acids and the 4-carboxybenzophenone triplet state in aqueous solution. **1994**, *98* (18), 4854-4860.
30. Hug, G. L.; Marciniak, B.; Bobrowski, K. Sensitized photo-oxidation of sulfur-containing amino acids and peptides in aqueous solution. *J. Photochem. Photobiol. A-Chem.* **1996**, *95* (1), 81-88.
31. Canonica, S.; Laubscher, H. U. Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants. *Photochem. Photobiol. Sci.* **2008**, *7* (5), 547-551.
32. Wenk, J.; von Gunten, U.; Canonica, S. Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical. *Environ. Sci. Technol.* **2011**, *45* (4), 1334-1340.
33. Wenk, J.; Canonica, S. Phenolic antioxidants inhibit the triplet-induced transformation of anilines and sulfonamide antibiotics in aqueous solution. *Environ. Sci. Technol.* **2012**, *46* (10), 5455-5462.
34. Canonica, S.; von Gunten, U.; Wenk, J. Reply to comment on "Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical". *Environ. Sci. Technol.* **2011**, *45* (18), 7947-7948.
35. Loeff, I.; Rabani, J.; Treinin, A.; Linschitz, H. Charge-transfer and reactivity of $n\pi^*$ and $\pi\pi^*$ organic triplets, including anthraquinonesulfonates, in interactions with inorganic anions: A comparative study based on classical Marcus theory. *J. Am. Chem. Soc.* **1993**, *115* (20), 8933-8942.
36. Bonneau, R.; Wirz, J.; Zuberbühler, A. D. Methods for the analysis of transient absorbance data. *Pure Appl. Chem.* **1997**, *69* (5), 979-992.
37. Treinin, A.; Hayon, E. Quenching of triplet states by inorganic ions. Energy transfer and charge transfer mechanisms. *J. Am. Chem. Soc.* **1976**, *98* (13), 3884-3891.
38. Shizuka, H.; Obuchi, H. Anion-induced triplet quenching of aromatic ketones by nanosecond laser photolysis. *J. Phys. Chem.* **1982**, *86* (8), 1297-1302.

39. Inbar, S.; Linschitz, H.; Cohen, S. G. Quenching, radical formation, and disproportionation in the photoreduction of 4-carboxybenzophenone by 4-carboxybenzohydrol, hydrazine, and hydrazinium ion. *J. Am. Chem. Soc.* **1981**, *103* (24), 7323-7328.
40. Hurley, J. K.; Linschitz, H.; Treinin, A. Interaction of halide and pseudohalide ions with triplet benzophenone-4-carboxylate - Kinetics and radical yields. *J. Phys. Chem.* **1988**, *92* (18), 5151-5159.
41. Moore, J. N.; Phillips, D.; Nakashima, N.; Yoshihara, K. Photochemistry of 9,10-anthraquinone-2,6-disulfonate. *J. Chem. Soc. Faraday Trans. 2* **1986**, *82*, 745-761.
42. Moore, J. N.; Phillips, D.; Hester, R. E. Time-resolved resonance Raman spectroscopy applied to the photochemistry of the sulfonated derivatives of 9,10-anthraquinone. *J. Phys. Chem.* **1988**, *92* (20), 5619-5627.
43. Hauke, F.; Hirsch, A.; Atalick, S.; Guldi, D. Quantitative transduction of excited-state energy in fluorophore-heterofullerene conjugates. *Eur. J. Org. Chem.* **2005**, (9), 1741-1751.
44. Lathioor, E. C.; Leigh, W. J. Bimolecular hydrogen abstraction from phenols by aromatic ketone triplets. *Photochem. Photobiol.* **2006**, *82* (1), 291-300.
45. Gorman, A. A.; Parekh, C. T.; Rodgers, M. A. J.; Smith, P. G. The quenching of the triplet states of aromatic carbonyl compounds by triethylamine: Solvent effects on correlations with the function $\{^3\Delta E_{O,O} + E(A^{\cdot-}/A)\}$. *J. Photochem.* **1978**, *9* (1), 11-17.
46. Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. Extent of charge transfer in the photoreduction of phenyl ketones by alkylbenzenes. *J. Am. Chem. Soc.* **1986**, *108* (24), 7727-7738.
47. Gamage, R. S. K. A.; McQuillan, A. J.; Peake, B. M. Ultraviolet-visible and electron paramagnetic resonance spectroelectrochemical studies of the reduction products of some anthraquinone sulfonates in aqueous solutions. *J. Chem. Soc.-Faraday Trans.* **1991**, *87* (22), 3653-3660.
48. Bensasson, R.; Goldschmidt, C. R.; Land, E. J.; Truscott, T. G. Laser intensity and the comparative method for determination of triplet quantum yields. *Photochem. Photobiol.* **1978**, *28* (2), 277-281.
49. Görner, H. Oxygen uptake and involvement of superoxide radicals upon photolysis of ketones in air-saturated aqueous alcohol, formate, amine or ascorbic acid solutions. *Photochem. Photobiol.* **2006**, *82* (3), 801-808.
50. Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. Time-resolved luminescence measurements of triplet-sensitized singlet-oxygen production: Variation in energy-transfer efficiencies. *J. Am. Chem. Soc.* **1984**, *106* (17), 4679-4682.
51. Hare, P. M.; Price, E. A.; Bartels, D. M. Hydrated electron extinction coefficient revisited. *J. Phys. Chem. A* **2008**, *112* (30), 6800-6802.
52. Wilkinson, F.; Helman, W. P.; Ross, A. B. Rate constants for the decay and reactions of the lowest electronically excited singlet state of molecular oxygen in solution - An expanded and revised compilation. *J. Phys. Chem. Ref. Data* **1995**, *24* (2), 663-1021.

- 533 53. Chin, Y. P.; Aiken, G.; Oloughlin, E. Molecular-weight, polydispersity, and spectroscopic
534 properties of aquatic humic substances. *Environ. Sci. Technol.* **1994**, *28* (11), 1853-1858.
- 535 54. Del Vecchio, R.; Blough, N. V. Photobleaching of chromophoric dissolved organic matter
536 in natural waters: kinetics and modeling. *Mar. Chem.* **2002**, *78* (4), 231-253.
- 537 55. Hiatt, C. W.; Kaufman, E.; Helprin, J. J.; Baron, S. Inactivation of viruses by the
538 photodynamic action of toluidine blue. *J. Immunol.* **1960**, *84* (5), 480-484.
- 539 56. Gerba, C. P.; Wallis, C.; Melnick, J. L. Disinfection of wastewater by photodynamic
540 oxidation. *Journal Water Pollution Control Federation* **1977**, *49* (4), 575-583.
- 541 57. Gerba, C. P.; Wallis, C.; Melnick, J. L. Application of photodynamic oxidation to
542 disinfection of tapwater, seawater, and sewage contaminated with poliovirus. *Photochem.*
543 *Photobiol.* **1977**, *26* (5), 499-504.
- 544 58. Acher, A. J.; Juven, B. J. Destruction of coliforms in water and sewage water by dye-
545 sensitized photooxidation. *Appl. Environ. Microbiol.* **1977**, *33* (5), 1019-1022.
- 546 59. Acher, A. J.; Saltzman, S. Dye-sensitized photooxidation of bromacil in water. *J. Environ.*
547 *Qual.* **1980**, *9* (2), 190-194.
- 548 60. Rejto, M.; Saltzman, S.; Acher, A. J.; Muszkat, L. Identification of sensitized
549 photooxidation products of s-triazine herbicides in water. *J. Agric. Food Chem.* **1983**, *31* (1),
550 138-142.
- 551 61. Kohn, T.; Nelson, K. L. Sunlight-mediated inactivation of MS2 coliphage via exogenous
552 singlet oxygen produced by sensitizers in natural waters. *Environ. Sci. Technol.* **2007**, *41* (1),
553 192-197.
- 554 62. Remucal, C. K.; McNeill, K. Photosensitized amino acid degradation in the presence of
555 riboflavin and its derivatives. *Environ. Sci. Technol.* **2011**, *45* (12), 5230-5237.

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